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THE ROLE OF THE DIPOLE-DIPOLE INTERACTION IN THE SOLVATION OF MONOATOMIC MONOVALENT IONS ON THE BASIS OF THE MEAN SPHERICAL APPROXIMATION

by

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The Role of Dipole-Dipole Interactions in the Solvation of Monoatomic Monovalent Ions in Water on the Basis of the Mean Spherical Approximation

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Dedicated to Professor Brian E. Conway on the occasion of his retirement.

Introduction

We have recently [1-3] analyzed thermodynamic data for the solvation of monoatomic monovalent ions in water and a number of other polar solvents on the basis of the mean spherical approximation (MSA) [4-6]. The attractive feature of the MSA is that it provides simple analytical results which can easily be used by those analyzing experimental data. An important departure of our work from that carried out earlier is that the polarization parameter λ which characterizes ion-solvent interactions is regarded as an adjustable parameter whose value is estimated from the experimental Gibbs solvation energy. This leads to the conclusion that λ depends not only on the nature of the solvent but also on the sign of the charge on the ion. Although this result is perhaps not surprising, it emphasizes that a model which considers only point charge-point dipole interactions cannot adequately describe experimental results. In other words, the statistical mechanical description of an electrolyte solution must include consideration of higher order moments, and the polarizability of the solvent. These features of the system are incorporated in a 'sticky' parameter [7] which reflects the fact that anions and cations bind differently to the solvent. Anions disrupt water structure very little, for example, whereas cations which are attracted to the electronegative oxygen atom cause local disruption of the solvent. It can be shown [7] that the effect of this sticky interaction is to change the value of the parameter, λ, so that instead of a single value of λ, which is derived for a mixture of ions in a solvent of hard dipoles, we have different values for each ionic species, λ_i. All deviations from the MSA will be lumped into this effective polarization parameter.

Our model of the electrolyte solution consists of a mixture of charged hard spheres of radius r_i (the ions) and hard spheres with a permanent point dipole of radius r_S. These molecules can also have a sticky dipole [7] interaction which may preferentially bind the anions or cations. Analysis of this system within the MSA leads to explicit expressions for the thermodynamic functions, in particular, the Gibbs energy of solvation. Our previous analysis [1-3] was based on the assumption that the dipole-dipole contribution could be neglected, the Gibbs energy of solvation being equated to the MSA estimate of the ion-dipole contribution. This assumption definitely affects the value of the polarization parameter estimated from experimental data, but confirmation that it is a reasonable approach was obtained when it was noted [2] that it leads to a reasonable separation of the components for cations and anions when experimental data for the alkali metal halides are examined. Nevertheless, a better description of the system is obtained when dipole-dipole interactions are considered.

In the present manuscript, the model used previously is extended to include consideration of dipole-dipole interactions. The Gibbs energy and entropy of solvation of the alkali metal and halide ions in water are reconsidered using the MSA model and the results are compared with those obtained earlier.

The Model

In the MSA for a system of spherical hard ions and dipoles of different sizes, the following expression is derived [8-12] for the ion-dipole contribution to the Gibbs energy of solvation in the limit of infinite dilution:

$$G_{id} = -\frac{N_0(z_i e_0)^2}{8\pi\varepsilon_0 r_i}\left(1 - \frac{1}{\varepsilon_s}\right)\frac{1}{(1+\xi_i)} \qquad (1)$$

Here, z_i, is the valence of the ion, e_0, the fundamental charge, ε_s, the static dielectric constant of the solvent, ε_0, the permittivity of free space, r_i, the radius of the ion, and N_0, the Avogadro constant. The dimensionless parameter ξ_i, which depends on the nature of the solvent and the ion, is given by

$$\xi_i = r_s/(\lambda r_i) \qquad (2)$$

where r_s is the radius of the solvent molecule represented as a sphere, and λ, the MSA polarization parameter. In earlier work [6-9], λ was calculated from the dielectric constant of the pure solvent ε_s using the Wertheim relationship [13]

$$\lambda^2 (\lambda+1)^4 = 16\,\varepsilon_s \qquad (3)$$

Although this value of the polarization parameter may be appropriate for estimating dipole-dipole interaction energy, it gives poor estimates of the Gibbs solvation energy when this is assumed to equal G_{id} [1-3] Thus, values of λ appropriate for cations and for anions were determined separately on the basis of experimental data for the alkali metal and halide ions, respectively. Thus, for a monovalent monoatomic cation, G_{id} is given by

$$G_{id}(C^{+}) = -\frac{N_o\,(z_i e_o)^2}{8\pi\varepsilon_o}\left(1 - \frac{1}{\varepsilon_s}\right)\frac{1}{(r_i+\delta_c)} \tag{4}$$

where

$$\delta_c = r_s/\lambda_c \tag{5}$$

λ_c being the corresponding cationic polarization parameter. Similarly, for monovalent monoatomic anions

$$G_{id}(A^{-}) = -\frac{N_o\,(z_i e_o)^2}{8\pi\varepsilon_o}\left(1 - \frac{1}{\varepsilon_s}\right)\frac{1}{(r_i+\delta_A)} \tag{6}$$

where

$$\delta_A = r_s/\lambda_A \tag{7}$$

and λ_A is the polarization parameter for the anion. In our simple theory, δ_A and δ_c are clearly adjustable parameters. The difference between them is due to the fact that real solvent molecules are non-spherical, and that there are specific chemical bonds between the ions and the solvent which are different for the cations and the anions. The difference could be interpreted to result from an attractive or repulsive sticky interaction, and/or a different distance of closest approach, or both. Thus,

use letters

$$\delta_i = \frac{r_s + \Delta_{si}}{\lambda} \qquad i = \cancel{A,C}\ C,A \tag{8}$$

Or, in other words,

$$\lambda_i = \frac{r_s}{r_s+\Delta_{si}}\,\lambda \qquad i = \cancel{A,C}\ C,A \tag{9}$$

The second contribution to the Gibbs solution energy comes from repulsive dipole-dipole interactions [10, 11] and is given by the equation

$$G_{dd} = \frac{(z_i e_o)^2(\varepsilon_s-1)^2}{64\pi\, \varepsilon_o \varepsilon_s\, r_i(1+\xi_i)^2} \left[\frac{4 + \xi_i\left(\frac{3\lambda+2}{\lambda+1}\right)}{\varepsilon_s + \frac{\lambda(\lambda+3)}{2(\lambda+1)^2}}\right] \tag{10}$$

Here, the parameter λ is assumed to be that given by the Wertheim equation, that is, the value appropriate for dipole-dipole interactions [10,11]. This expression may be simplified considerably when one considers the range of values typical for λ. For water whose dielectric constant is 78.3 at 25 °C, λ is equal to 2.65. The corresponding value of the ratio $\lambda(\lambda+3)/2(\lambda+1)^2$ which appears in the denominator of the term in square brackets in eq. (10) is 0.56. This is negligible with respect to the value of ε_s and may be neglected. The ratio appearing in the numerator of this term, namely, $(3\lambda+2)/(\lambda+1)$ is equal to 2.7. Thus, the expression for G_{dd} may be rewritten as

$$G_{dd} = \frac{N_o(z_i e_o)^2}{64\pi\, \varepsilon_o r_i}\left(1 - \frac{1}{\varepsilon_s}\right)^2 \frac{(4+2.7\,\xi_i)}{(1+\xi_i)^2} \tag{11}$$

The simplified expression has the advantage that the parameter λ does not appear on its own but only in the ratio ξ_i. This fact is important in applying the expression to experimental data. Finally, on the basis of previous work [11] only a fraction θ of the dipole-dipole term is used in estimating the Gibbs energy of solvation so that the final expression for G_s becomes

$$G_s = G_{id} + \theta\, G_{dd} \tag{12}$$

The expressions for the corresponding entropies are obtained from the temperature derivatives of the above Gibbs energies. For the ion-dipole term, the result for a cation is

$$S_{id}(C^+) = \frac{N_o(z_i e_o)^2}{8\pi\, \varepsilon_o}\left[\frac{1}{\varepsilon_s^2}\frac{d\varepsilon_s}{dT}\frac{1}{(r_i+\delta_c)} - \frac{1}{(r_i+\delta_c)^2}\left(1 - \frac{1}{\varepsilon_s}\right)\frac{d\delta_c}{dT}\right] \tag{13}$$

where $d\delta_c/dT$ is the temperature derivative of δ_c which is obtained from the temperature derivative of λ_c. Comparing eqs. (4) and (13), it is easily shown that

$$S_{id}(C^+)\left(1 - \frac{1}{\varepsilon_s}\right) = -\frac{G_{id}(C^+)}{\varepsilon_s^2}\frac{d\varepsilon_s}{dT} - \frac{8\pi\, \varepsilon_o G_{id}^2(C^+)}{N_o(z_i e_o)^2}\frac{d\delta_c}{dT} \tag{14}$$

The corresponding expression for an anion is

$$S_{id}(A^-)\left(1 - \frac{1}{\varepsilon_s}\right) = -\frac{G_{id}(A^-)}{\varepsilon_s^2}\frac{d\varepsilon_s}{dT} - \frac{8\pi\,\varepsilon_0 G_{id}^2(A^-)}{N_0(z_i e_0)^2}\frac{d\delta_A}{dT} \tag{15}$$

From these equations it follows that two additional parameters are required to estimate the entropy of solvation of a salt, namely, the temperature derivatives of the polarization parameters for the cation and anion.

From the expression for G_{dd}, one obtains the following equation for the corresponding entropy:

$$S_{dd} = G_{dd}\left[\frac{2}{\varepsilon_s^2}\frac{d\varepsilon_s}{dT} \Big/ \left(1 - \frac{1}{\varepsilon_s}\right) + \frac{2.7\,\xi_i}{\lambda}\frac{d\lambda}{dT} \Big/ (4 + 2.7\,\xi_i) - \frac{2\xi_i}{\lambda}\frac{d\lambda}{dT} \Big/ (1 + \xi_i)\right] \tag{16}$$

The derivative $d\lambda/dT$ may be found from the Wertheim equation from which one obtains

$$\frac{d\lambda}{dT} = \left[\frac{\lambda(1+\lambda)}{3\lambda+1}\right]\frac{1}{2\varepsilon_s}\frac{d\varepsilon_s}{dT} \tag{17}$$

Assuming that the fraction θ is independent of temperature, the resulting expression for the entropy of solvation is

$$S_s = S_{id} + \theta\, S_{dd} \tag{18}$$

This model is now examined with respect to data for monoatomic monovalent ion solvation in water.

Results and Discussion

In order to apply the above model to experimental data one must choose radii for the ions and an extrathermodynamic assumption for extracting single ion solvation energies from experimental values for the salts, namely, the alkali metal halides. Two sets of ionic radii give good fits between experiment and theory [2], namely, the values given by Pauling [14] and those extracted from neutron and X-ray diffraction experiments [15]. The Pauling values are used here simply because they are more familiar. The extrathermodynamic assumptions used to separate experimental quantities into those for cations and anions were examined in detail for aqueous systems by Conway [16]. Values of the Gibbs energy and entropy of solvation for the alkali metal cations and halide anions estimated by Conway are summarized in Table 1 together with their Pauling radii.

In our previous analysis of the Gibbs solvation energy [1,2] the contribution of dipole-dipole interactions was ignored ($\theta = 0$ in eq. (12)). Analysis of the data for the alkali metal halides showed that the best values of δ_c and δ_A (eqs. (4) and (6)) assuming Pauling radii for the ions were 82.4 and 18.0 pm, respectively [2]. The quality of the fit between theory and experiment is really excellent, the standard deviation for the calculated values being 1.5 kJ mol^{-1}, that is, significantly less than 1 percent. This result is illustrated in Fig. 1 in terms of a plot of $-G_s$ against $1/(r_i+\delta_i)$. It is apparent that the values of G_s fit very well on a straight line in the region where data exist but that the slope of the best straight line through these data is slightly higher (75.2 kJ nm mol^{-1}) than that predicted by theory (69.45 kJ nm mol^{-1}). As a result, an ion with infinite radius is predicted to have a Gibbs solvation energy of 35.7 kJ mol^{-1} when this simple model is applied. This can be attributed to the failure to account for dipole-dipole interactions which constitute a positive contribution to G_s.

The same data were re-examined on the basis of eq. (12) using the expression for G_{dd} given by eq. (11). The fit was carried out so that the resulting estimates of G_{id} and G_{dd} would go to zero for an ion of infinite radius. The resulting best values of δ_c and δ_A were much smaller than those obtained by the simpler analysis, and are recorded in Table 2. The corresponding estimates of G_{id} are plotted against $1/(r_i+\delta_i)$ in Figure 2. As expected these estimates are larger in magnitude than the experimental values of G_s also plotted on the same graph. Both plots are linear in $1/(r_i+\delta_i)$ and have zero intercepts within the experimental standard deviation. Estimates of θG_{dd} for the same nine ions are also plotted in this figure. For the cations, this quantity varies from a high of 41.2 kJ mol^{-1} for Li^+ to a low of 22.7 kJ mol^{-1} for Cs^+, and is approximately eight percent of the magnitude of G_{id}. In the case of the anions it represents a slightly higher fraction of the total Gibbs energy and varies from a high of 42.7 kJ mol^{-1} for F^- to a low of 30.8 kJ mol^{-1} for I^- ion. The values of θG_{dd} are also approximately linear in $1/(r_i+\delta_i)$ with an intercept corresponding to zero for an infinitely large ion. The value of δ used in estimating G_{dd} is that estimated on the basis of the Wertheim equation, namely, 51.6 pm. When the contributions, G_{id} and θG_{dd} are added one obtains estimates of G_s which agree with those obtained from experimental data to within a few kJ

mol^{-1}. Values of the parameters used in our calculations including the fraction θ are summarized in Table 2.

A successful model for ionic solvation must also be able to estimate correctly the entropy of solvation. In order to make this calculation one must have estimates of the temperature derivatives of the parameters δ_c, δ_A and λ. The latter was calculated using eq.(15) which gives a value of $-2.48 \times 10^{-8}\ K^{-1}$ for $d\lambda/dT$ on the basis of the dielectric properties of water. Assuming r_s, the radius of a water molecule, is equal to 137 pm the corresponding value of $d\delta/dT$ is 0.048 pm K^{-1}. Values of δ_c and δ_A were determined from the single ion estimates of S_s given by Conway [15]. In the case of cations on the basis of eqs. (14) and (18), one may write

$$Y = \frac{d\delta_c}{dT} X \tag{19}$$

where

$$X = -\frac{8\pi\, \varepsilon_o G_{id}{}^2(C^+)}{N_o(z_i e_o)^2} \tag{20}$$

and

$$Y = S_s(C^+)\left(1 - \frac{1}{\varepsilon_s}\right) + \frac{G_{id}(C^+)}{\varepsilon_s{}^2}\frac{d\varepsilon_s}{dT} + \theta S_{ss} \tag{21}$$

$S_c(C^+)$ being the solvation entropy of the cation. Similar equations can be written for anions using eqs. (15) and (18). A plot of Y against X for both ions is shown in Fig. 3. These data were fit to a straight line passing through zero (one parameter fit) as shown, the resulting slope, which equals both $d\delta_s/dT$ and $d\delta_A/dT$, being 0.032 pm K^{-1}. It is important to note that the present analysis suggests that these temperature coefficients are equal in contrast to our previous conclusion based on an analysis which ignored dipole-dipole interactions. The estimated error in the slope is not large, being about 4%. It should also be noted that the magnitude of $d\delta_c/dT$ and $d\delta_A/dT$ is about 65 percent of that found on the basis of the Wertheim equation (eq. (17)).

Using the above coefficients values of S_{id} were estimated for the alkali metal and halide ions and are plotted in Fig. 4 together with estimates of S_{dd} and experimental values of S_s against the experimental Gibbs solvation energy G_s. It is clear that the entropy of solvation is approximately a quadratic function of the Gibbs energy as suggested by the MSA model.

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Table 1. Pauling radii and standard thermodynamic parameters of solvation of monoatomic monovalent ions in water at 298° K

	Ion	Pauling Radius r_i, nm	Gibbs Solvation energy G_s/kJ mol^{-1}	Solvation Entropy S_s/J K^{-1} mol^{-1}
1.	Li^+	0.060	-487.5	-141
2.	Na^+	0.095	-387.6	-109.7
3.	K^+	0.133	-314.0	- 74.2
4.	Rb^+	0.148	-292.7	- 62.1
5.	Cs^+	0.169	-260.5	- 59.1
6.	F^-	0.136	-456.8	-136.8
7.	Cl^-	0.181	-339.7	- 79.9
8.	Br^-	0.195	-325.9	- 64.4
9.	I^-	0.216	-279.5	- 41.4

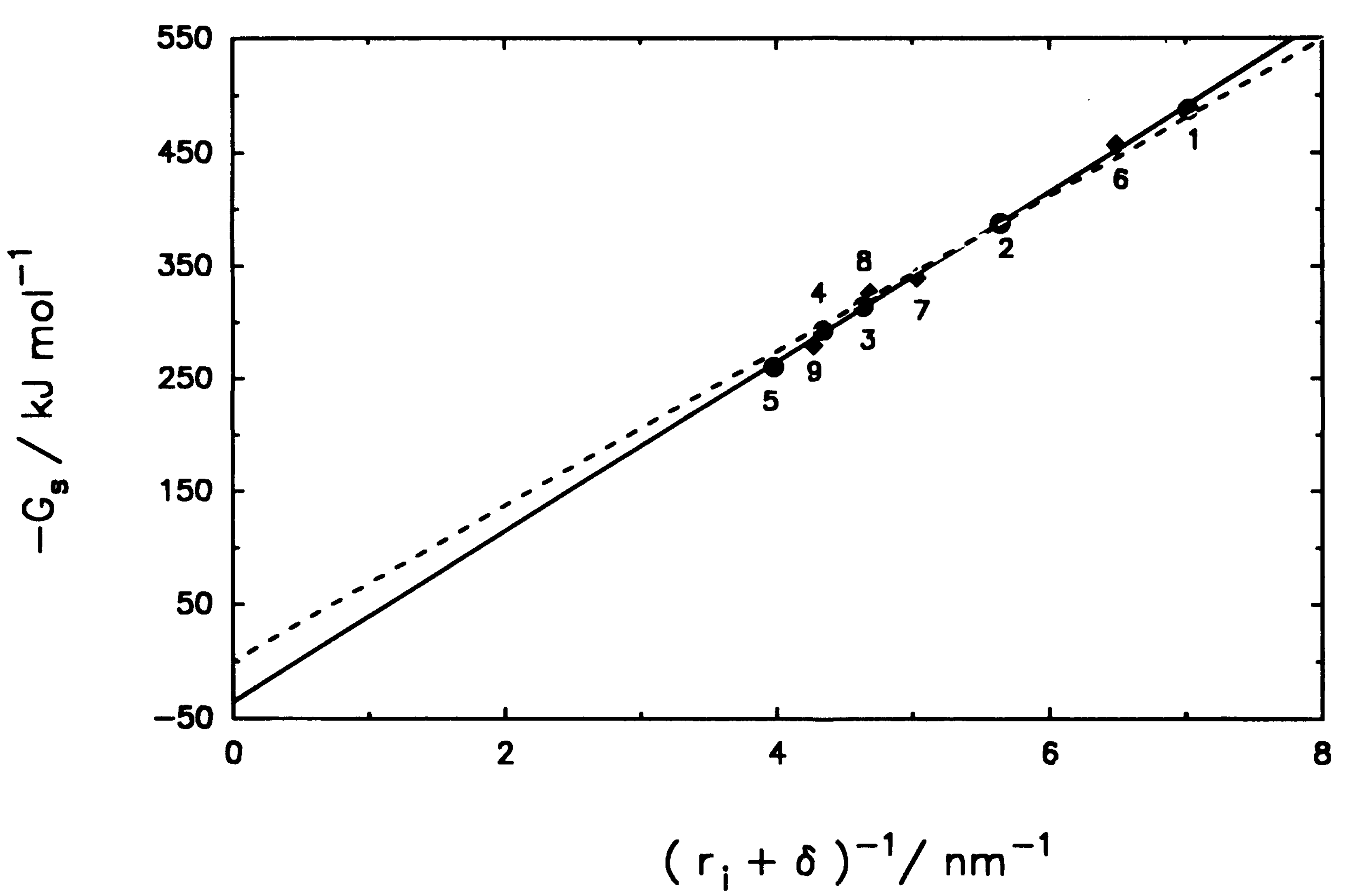
Legends for Figures

Figure 1. Plot of the single ion Gibbs energy of solvation for the alkali metal cations (●) and halide anions (♦) against the reciprocal of the ion radius, r_i, plus the MSA parameter δ. The value of δ for cations was 82.4 pm and for anions, 18.0 pm. The solid line shows the least squares fit to these data, and the broken line the value of the ion-dipole contribution to the Gibbs energy according to eqs. (4) and (6). The numbers refer to individual ions listed in Table 1.

Figure 2. Plot of the single ion Gibbs energy of solvation, G_s, the ion-dipole contribution, G_{id}, and the dipole-dipole contribution, G_{dd}, against the reciprocal of the ion radius r_i plus the MSA parameter δ for the alkali metal cations (●, o) and halide anions (♦, ◊). The value of δ for cations was 69.2 pm, and for anions, 1.1 pm. The solid lines show the least squares fit to each set of data. The numbers refer to individual ions listed in Table 1.

Figure 3. Plot of the function, Y, (eq. (17)) against the function X (eq. (18)) for the alkali metal cations (●) and halide anions (♦). The solid line was determined by a one parameter least squares fit going through the origin. The numbers refer to individual ions listed in Table 1.

Figure 4. Plot of the single ion entropy of solvation, S_s, the ion-dipole contribution, S_{id}, and the dipole-dipole contribution, S_{dd}, against the Gibbs energy of solvation G_s for the alkali metal cations (●, o) and halide anions (♦, ◊). The curves are fitted to data for S_{id} and S_{dd}. The numbers refer to individual ions listed in Table 1.



550
450
350
250
150
50
−50
0
2
4
6
8
1
2
3
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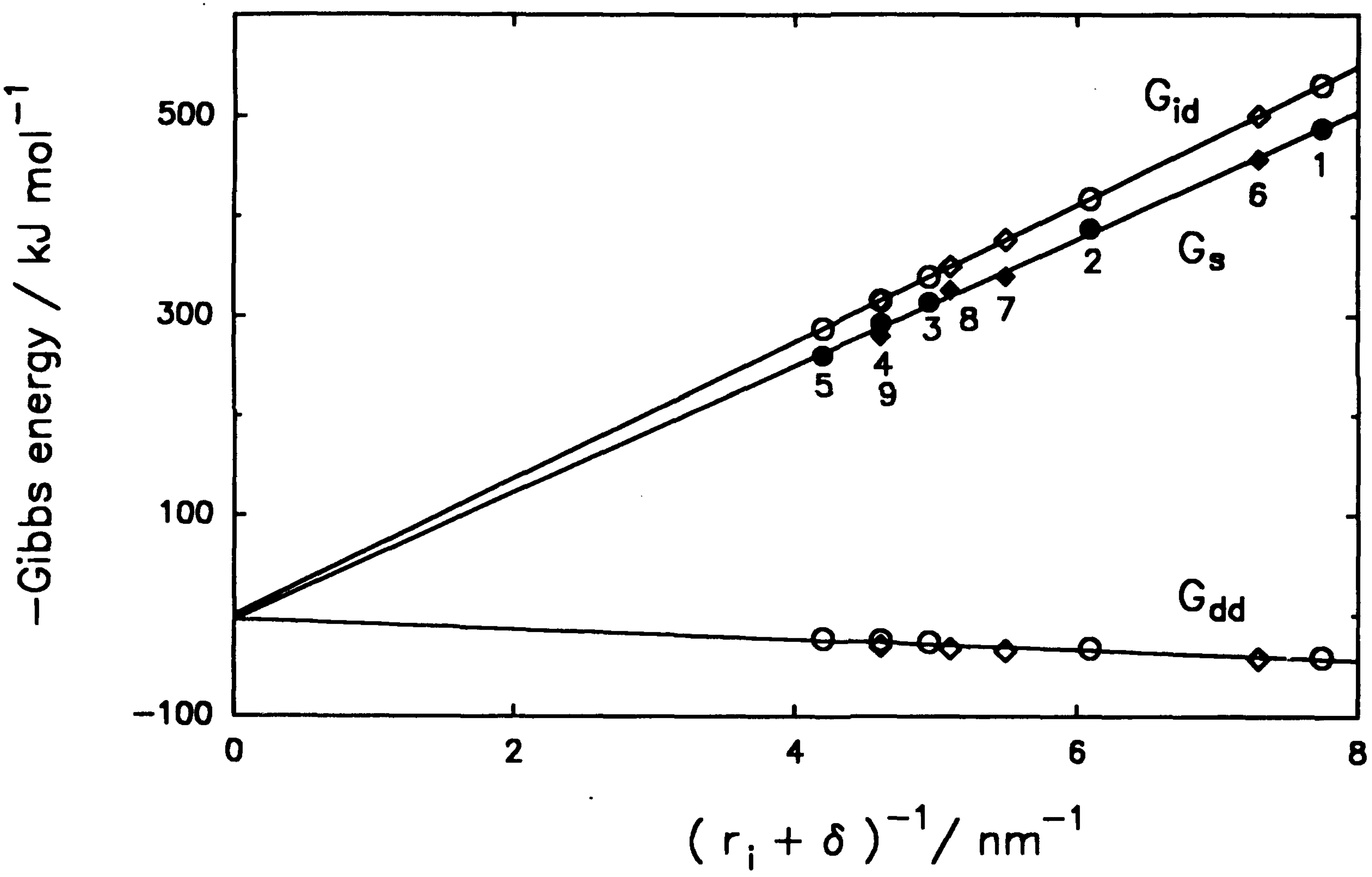
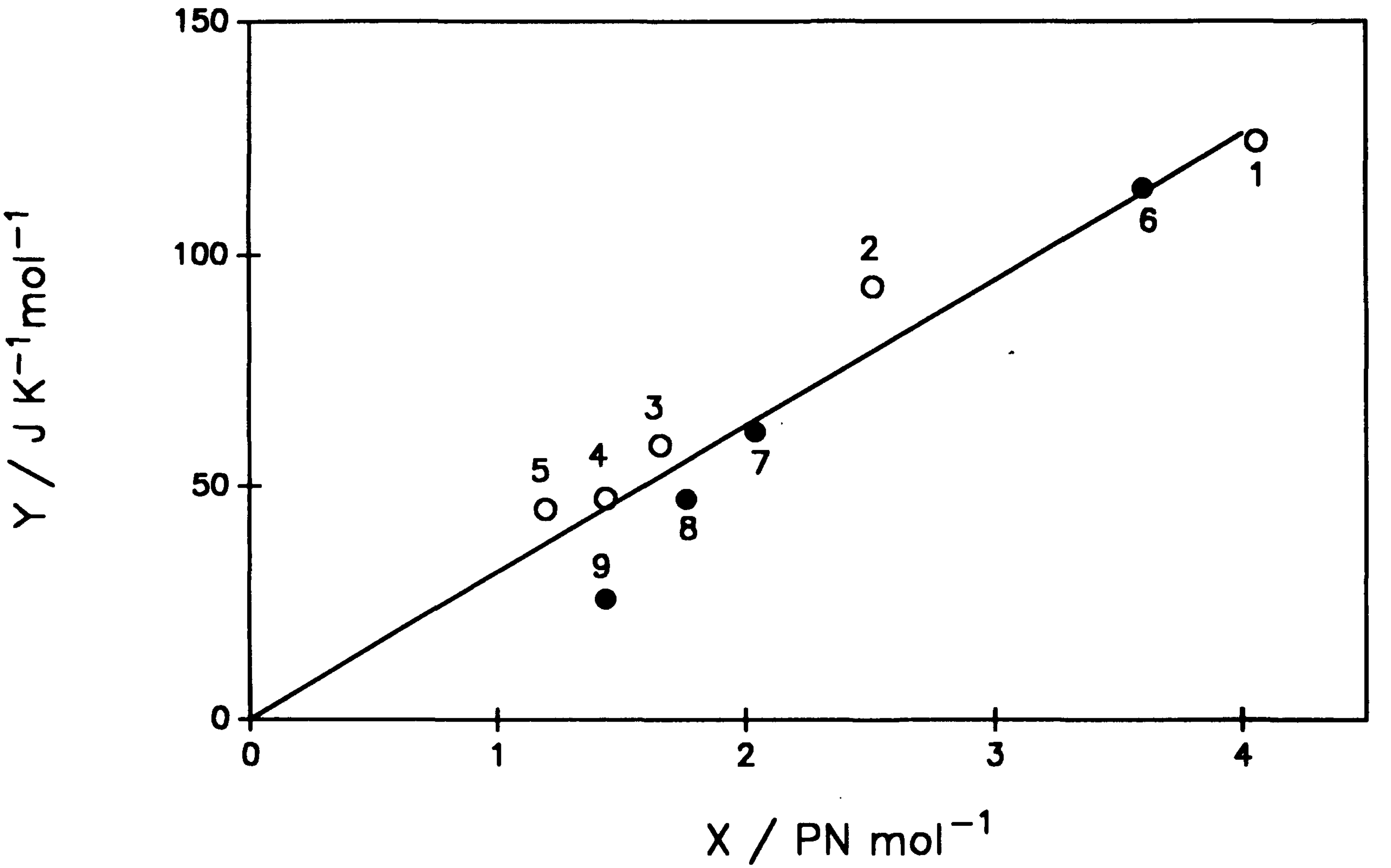
6
7
8
9
$-G_s$ / kJ mol^{-1}
$(r_i + \delta)^{-1}$ / nm^{-1}

Fig.1



-Gibbs energy / kJ mol^-1
500
300
100
-100
0
2
4
6
8
(r_i + δ)^-1 / nm^-1
G_id
G_s
G_dd
1
2
3
4
5
6
7
8
9

Fig 2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100
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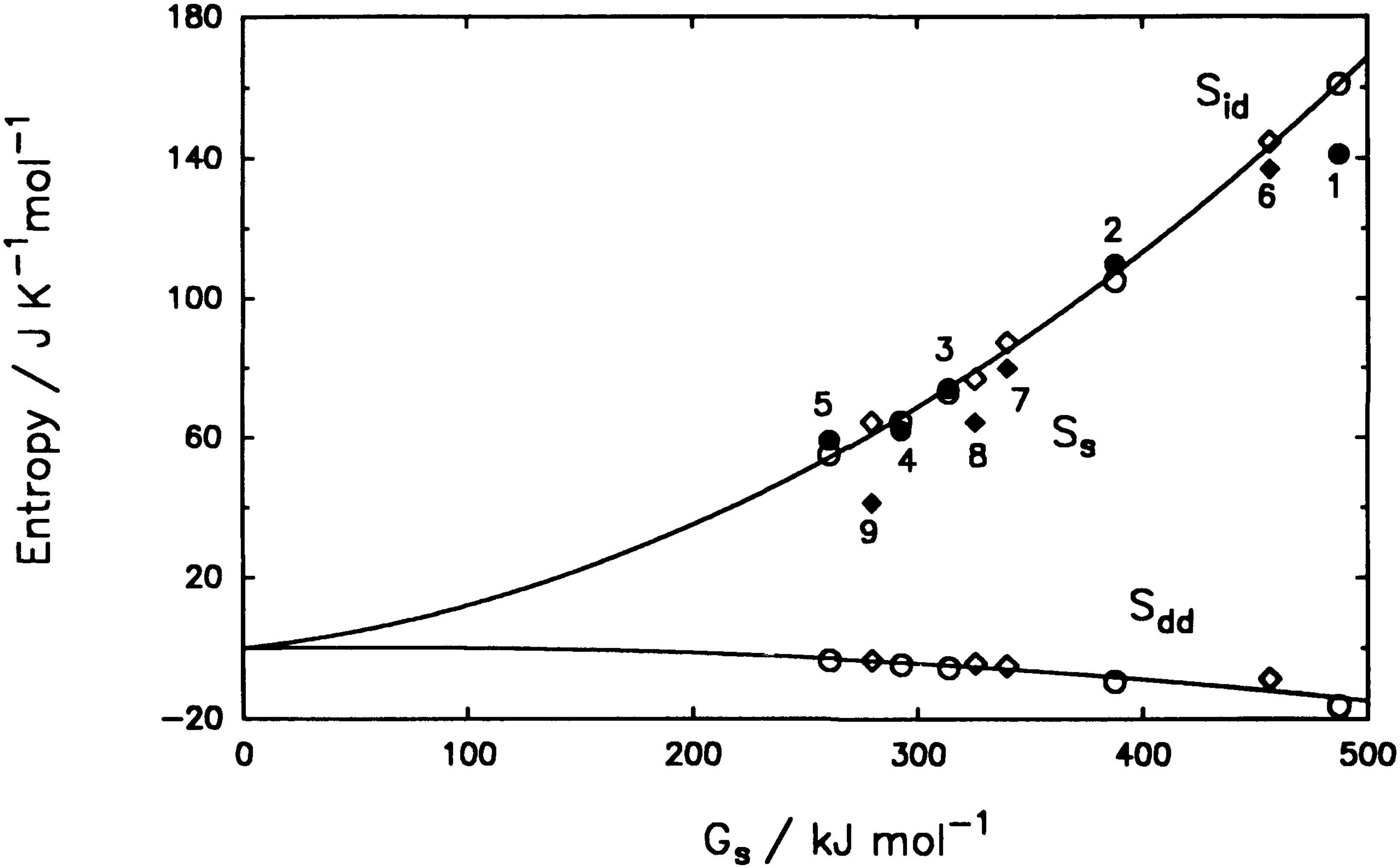
Y / J K⁻¹mol⁻¹
X / PN mol⁻¹



Entropy / J K⁻¹mol⁻¹
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140
100
60
20
−20
0
100
200
300
400
500
G_s / kJ mol⁻¹
S_id
S_s
S_dd
1
2
3
4
5
6
7
8
9